

AIR CONTENT DETERMINATION

Field of the Invention

5 This invention relates generally to devices and methods for the detection of atmospheric components and, in particular, to devices and methods for the detection of nitrogen dioxide, nitrogen monoxide and ozone.

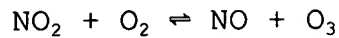
Background

10 In recent years, with increased concern over environmental issues, there is more and more need for accurate and cost effective measurement devices and methods for the detection of gases in the atmosphere. There is a demand both for measurements of pollutant
15 gases at ground level, due to their direct effect on human health, and also within the atmosphere for atmospheric analysis and research.

Ozone, nitrogen dioxide and nitrogen monoxide are gases of particular relevance and it is desirable to
20 monitor concentrations of these gases in air. Particular applications include roadside monitoring and atmosphere content monitoring.

The paper "Indirect Determination of Nitrogen Oxides by Chemiluminescence Techniques" (R. Guicherit, Atmos
25 Environ. 1972 Nov; 6(11) p.807-14) shows a method and apparatus for determining nitrogen dioxide in air samples. This process involves use of a chemiluminescent

detection system for ozone, which is produced by means of the effect of ultraviolet light on the equilibrium reaction:



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Ultraviolet light pushes the equilibrium to the right, forming nitrogen monoxide and ozone. This process involves irradiating a gas sample with ultraviolet light and then determining the final ozone concentration.

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The resulting system is complex and the authors found it essential to pass incoming gas through scrubbers to remove ozone and to oxidise nitrogen monoxide to nitrogen dioxide before beginning irradiation.

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This system further proposed that, once nitrogen dioxide had been determined, the concentration of nitrogen monoxide could subsequently be calculated after a separate reading of ozone produced by ultraviolet irradiation of a separate gas sample, scrubbed as before, with the addition of a further scrubber to remove ozone.

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Another known technique for determining total nitrogen oxide content in air is described in US Patent 3,973,914 to van Heusden. This functions by converting nitrogen dioxide to nitrogen monoxide which is then determined by monitoring chemiluminescence of the reaction between nitrogen monoxide and excess ozone.

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This process is the basis of a number of gas monitoring devices on sale at the present time. However, these devices are expensive (in the order of £10,000), complex and suffer from limitations, particularly relating to the quantitative conversion of nitrogen dioxide to nitrogen monoxide.

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A first aim of the present invention is to provide a cheaper, simpler and more reliable gas monitoring device, capable of accurate determination of nitrogen dioxide, nitrogen monoxide and/or ozone in air.

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One use for a cheaper, simple and more reliable gas monitoring device would be for measuring atmospheric

composition at high altitudes. Typically, this is carried out by attaching sensors to a helium filled weather balloon and to launch the balloon into the atmosphere. The sensor then transmits data, usually via
5 a radio link, as the balloon passes up through the atmosphere. The fact that the sensor is attached to a balloon places severe restrictions in terms of weight and cost on the sensor design. The cost aspect can be particularly critical, because generally such sensors
10 have to be treated as disposable, given that they may be difficult to locate once they fall back to the ground. All of this can make it extremely difficult to produce a sensor which provides appropriately accurate readings that are continuous throughout the ascent of the balloon
15 and which is capable of resisting the effects of high altitude and low temperature, where contaminants such as rain ice can affect sensor output.

Therefore, a second aim of the present invention is to provide a device that is suitably reliable, cheap and
20 light to benefit high altitude gas monitoring.

Furthermore, high altitude gas measurement systems usually use a pump to draw air into a sensing arrangement. The pumps are expensive, relatively heavy and require considerable power to operate, increasing
25 overall device weight.

Furthermore, with such sensors it can often be difficult to provide accurate readings because it is difficult to determine exactly the rate at which atmospheric air is flowing over the sensor and a further
30 aim of the present invention is to provide sensing apparatus which mitigates this problem.

Summary of the Invention

According to a first aspect of the present
35 invention, there is provided an instrument for assaying the concentration of one or more of nitrogen dioxide, nitrogen monoxide and/or ozone in an air sample; the instrument comprising an equilibrium altering means for

changing, or an element adapted to change, the equilibrium between nitrogen monoxide and nitrogen dioxide in the presence of ozone and oxygen, and a first gas sensor for quantifying the concentration of a first
5 gas, being one of nitrogen dioxide, nitrogen monoxide or ozone; the instrument being adapted to measure the concentration of the first gas whilst the equilibrium between nitrogen monoxide and nitrogen dioxide in the presence of ozone and oxygen is altered and thereby to
10 calculate the concentration of nitrogen dioxide, nitrogen monoxide and/or ozone in the air sample.

Preferably, the equilibrium altering means comprises an ultraviolet light source. More preferably, the ultraviolet light source is switched on and off
15 periodically.

The equilibrium altering means may comprise a means for adding, or an element adapted to add, one or more of nitrogen monoxide, nitrogen dioxide or ozone, and/or a means for removing, or an element adapted to remove, one
20 or more of nitrogen monoxide, nitrogen dioxide, ozone or oxygen.

Preferably, the instrument is adapted to measure the concentration of the first gas at a plurality of time points and thereby monitor the rate at which the balance
25 between nitrogen dioxide and nitrogen monoxide changes in response to the effects of the equilibrium altering means.

Typically, the first gas sensor is an ozone sensor.

The instrument may be adapted to allow for the
30 effects of temperature and/or pressure on the equilibrium between nitrogen dioxide and nitrogen monoxide.

According to a second aspect of the present invention there is provided a method of calculating the
35 concentration of nitrogen dioxide, nitrogen monoxide and/or ozone in air, the method comprising the steps of:

activating an equilibrium altering means for changing, or an element adapted to change, the

equilibrium between nitrogen monoxide and nitrogen dioxide in the presence of ozone and oxygen in an air sample;

5 taking three or more readings of the concentration of a first gas, being one of nitrogen dioxide, nitrogen monoxide or ozone including at least one reading taken before the changes caused by the equilibrium altering means reach a steady state; and

10 thereby calculating the concentration of nitrogen dioxide, nitrogen monoxide and/or ozone in the air sample.

Preferably, the equilibrium altering means is an ultraviolet light source.

15 Preferably, the method includes the step of switching the ultraviolet source on and off periodically.

The equilibrium altering means may comprise a means for adding, or an element adapted to add, one or more of nitrogen monoxide, nitrogen dioxide or ozone.

20 The equilibrium altering means may comprise a means for removing, or an element adapted to remove, one or more of nitrogen monoxide, nitrogen dioxide, ozone or oxygen.

25 The concentration of the first gas at a plurality of time points may be used to calculate the rate at which the balance between nitrogen dioxide and nitrogen monoxide changes in response to the effects of the equilibrium altering means.

The readings may be of ozone concentration.

30 The method may further include the step of allowing for the effects of temperature and/or pressure on the equilibrium between nitrogen dioxide and nitrogen monoxide.

35 According to a third aspect of the present invention there is provided a computer program comprising program instructions which, when loaded onto a computer, are adapted to calculate, or constitute a processing means for calculating, the concentration of nitrogen monoxide,

nitrogen dioxide and/or ozone in an air sample by the method of the second embodiment.

According to a fourth aspect of the present
5 invention there is provided a computer program according to the third aspect embodied on a record medium.

According to a fifth aspect of the present invention there is provided sensing apparatus for detecting
10 components in atmospheric air as the sensor is drawn up through the atmosphere, the sensor comprising:

a sensor element;

shielding means for shielding, or an element adapted to shield, the sensor element from direct contact with
15 air flow as the sensor is drawn through the atmosphere; and

means for diverting, or an element adapted to divert, air through the shielding means and over the sensor element as the sensor passes through the
20 atmosphere.

Preferably, the means for diverting air comprises a gas conducting member shaped to provide a pressure differential across the shielding means and cause air to move through the shielding means.

25 The gas conducting member may be shaped to provide a low pressure region at an entry to the shielding means and thereby draw air through the shielding means into the gas conducting member.

The gas conducting member may comprise a flow
30 restricting member for diverting air that flows through the gas conducting member in use into the shielding means.

The sensing apparatus may have an aperture to allow water or ice to flow out of the gas conducting member.

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According to a sixth aspect of the present invention there is provided sensing apparatus comprising:

a sensor element;

means for regulating, or an element adapted to regulate, the temperature of the sensor element by providing heat energy to the sensor element; and
means for calculating the air flow across the sensor element from the amount of heat energy supplied to the sensor element.

The sensor apparatus may further comprise a means for measuring, or an element adapted to measure, the temperature of the sensor.

Description of the Figures

Examples of the present invention will now be described with reference to the accompanying drawings, in which:

Figure 1 is a schematic diagram of an analytical system according to the present invention;

Figure 2 shows the response with time of ozone concentration in response to periodic ultraviolet irradiation, J;

Figure 3 shows the simulated variation of ozone, nitrogen monoxide and nitrogen dioxide concentrations in response to specific changes to the level of ultraviolet irradiation;

Figure 4 shows the simulated variation of ozone, nitrogen monoxide and nitrogen dioxide concentrations in response to specific periodic changes to the level of ultraviolet irradiation;

Figure 5 is a schematic cross-section through an example sensing apparatus;

Figure 6 is an expanded view of a section of Figure 5;

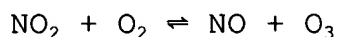
Figure 7 is a schematic cross-section through an alternative sensing apparatus; and

Figure 8 is a schematic cross-section through a further sensing apparatus.

Detailed Description of the Invention

Figure 1 shows an example analytical system according to the present invention. The analytical system shown generally as **1** comprises an air inlet **2** which allows an air sample to enter irradiation chamber **3**. The irradiation chamber **3** comprises an ultraviolet source **4** and may be encased by an ultraviolet reflective surface **13** such as a metal foil. There is a chamber outlet **5** from the irradiation chamber, which incorporates a UV light trap **6**. Air passes from the chamber outlet **5** to an external outlet **7** via an ozone sensor **10**. A pump (not shown) or airflow control means as discussed below may be provided to draw air through the external outlet **7** and through the sensor as a whole.

Within the irradiation chamber, ultraviolet light from the ultraviolet source **4** irradiates the air sample, driving the below reaction towards the formation of ozone and nitrogen monoxide:

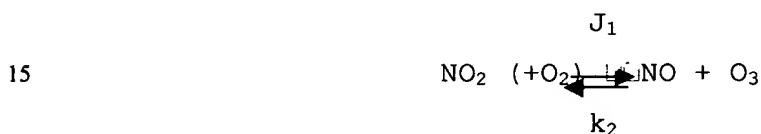


By positioning an ozone sensor **10** downstream from the ultraviolet source **4**, readings can be taken of ozone levels after the equilibrium has been affected by irradiation (or other means discussed below).

A processing means **20** such as a computer, microprocessor or other device having storage and processing capacity is provided to analyse the measurements and compute gas concentrations in the input gas sample. The invention further extends to the software used by said processing means **20** to control the switching on and off of the ultraviolet light source, record gas concentration readings from the sensor **10** and carry out gas concentration calculations. Said software may be provided on a digital storage means such as a magnetic or optical disk or solid state storage device such as EEPROM.

The basis of the present invention is that readings of ozone concentration are taken not simply after the ratio of nitrogen monoxide to nitrogen dioxide has been modified by the influence of ultraviolet light or other factors and a steady state has been reached, but also either (a) during the process of this ratio being altered or (b) after or during the application of two different means for altering the ratio. The resulting readings are then used to calculate the concentrations of nitrogen monoxide, nitrogen dioxide and ozone in the gas sample.

The kinetics of the underlying reaction can be summarised as follows:



$$d[\text{O}_3] / dt = J_1[\text{NO}_2] - k_2 [\text{NO}][\text{O}_3]$$

where $[\text{O}_3]$ is the instantaneous concentration of ozone, $[\text{NO}_2]$ is the instantaneous concentration of nitrogen dioxide, $[\text{NO}]$ is the instantaneous concentration of nitrogen monoxide, J_1 is rate coefficient for photolysis of NO_2 , in units of per second, and k_2 is the rate constant for the reverse reaction.

At equilibrium steady state:

$$[\text{O}_3] = J_1[\text{NO}_2] / k_2 [\text{NO}]$$

Characteristic time, τ , to equilibrium is given by:

$$\tau = (J_1 + k_2 [\text{NO}])^{-1}$$

Both equilibrium steady state ozone concentration and characteristic time can be readily deduced either from

monitoring the ozone concentration curve with time or from several individual ozone readings at different times by well-known mathematical methods.

5 Case 1 : in the sunlit atmosphere:

Typically $[O_3] = 50$ ppb - in excess over NO

$$J_1 = J_{\text{sunlight}} (= 10^{-2} \text{ s}^{-1})$$

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$$\tau = (10^{-2} + 5 \times 10^{-4} [\text{NO}] (\text{ppb}))^{-1} \text{ s},$$

and so $\tau < 100$ secs

15 Case 2: in the instrument under photolysis:

$$J_1 = J_{\text{NO}_2} (= 0.1 \text{ s}^{-1})$$

$$\tau = (10^{-1} + 5 \times 10^{-4} [\text{NO}])^{-1}$$

20

and so $\tau < 10$ secs

Case 3: in the dark:

25 $J_1 = 0$

Therefore, in the dark, the atmospheric steady state relaxes towards a state where $[\text{NO}]$ (or O_3) tends to zero with $\tau = (5 \times 10^{-4} [\text{NO}])^{-1}$ or $(5 \times 10^{-4} [\text{O}_3])^{-1}$ depending on

30 which gas is present in excess. Therefore, typically $\tau > (2.5 \times 10^{-2})^{-1} > 40$ secs. If, however, concentrations of $[\text{NO}]$ and $[\text{O}_3]$ are similar, it will be clear to one

skilled in the art that you instead get a complex but mathematically definable rate of ozone loss.

By monitoring the ozone concentration in response to periodic light and dark and application of standard
5 computing techniques it is therefore possible to get information about all three components $[O_3]$, $[NO_2]$ and $[NO]$.

In a preferred embodiment, light is pulsed as shown in Figure 2 which illustrates the periodic alteration of
10 J with time and the resulting ozone concentration. Clearly the precise pulse shape of ozone concentration will depend on the gas flow rate, length of the ultraviolet irradiation zone, spectrum and intensity of ultraviolet source, gap between the end of irradiation
15 zone and sensor and other calculable parameters.

Therefore, $d[O_3]/dt$ under instrument irradiation can be used to give the concentration of nitrogen dioxide in the air sample.

Measurement of ozone concentration after short
20 sample time in dark gives the ozone concentration in the air sample.

The concentration of ozone after full relaxation in the dark gives the difference between sample ozone and nitrogen monoxide concentrations.

25 The characteristic relaxation time in the dark of an unphotolysed air sample gives the nitrogen monoxide concentration.

The characteristic relaxation time of a photolysed air sample gives the sum of the concentrations of
30 nitrogen monoxide and nitrogen dioxide.

The time resolved measurement of ozone therefore allows rates and relaxation time to be determined and so the concentrations of nitrogen monoxide, nitrogen dioxide and ozone can be determined.

Temperature has an effect on the value of J_1 . The corresponding chemical step has a small activation energy thus temperature effects are small. If
5 temperature effects need to be corrected this can be done using a simple measurement of temperature from a temperature measuring means (not shown). Pressure will have a still smaller effect and will preferably not be taken into account; however, it could be readily
10 corrected for if required using readings from a pressure gauge (not shown). Pressure has a linear effect on the measured concentration for some types of ozone sensor as the partial pressure of ozone changes linearly with pressure but the concentration of ozone does not. This
15 can readily be allowed for by well known software methods.

Low frequency phase sensitive detection might allow determination of relaxation time and the information can be processed to give improved sensitivity.

20 Figure 3 and 4 show the concentration of nitrogen monoxide, nitrogen dioxide and ozone with time (in seconds) for various simulated experiments at 298 Kelvin, 1 atmosphere pressure, $k = 0.06$ per second.

In these calculations, it is recognised the
25 underlying chemical reactions are:

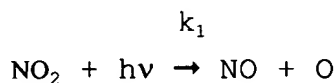


Figure 3a shows the response to 20 seconds in the dark
35 and 30 seconds of photolysis starting with initial gas

concentrations of 30 ppb NO₂, 10 ppb NO and 50 ppb O₃.

Figure 3b shows the equivalent situation starting with 30 ppb NO₂, 10 ppb NO and 0.5 ppb O₃.

Figures 3c and 3d show the equivalent ozone and nitrogen dioxide concentrations with time for starting concentrations 30 ppb NO₂, 0.5 ppb NO, 0.5 ppb O₃ (3(c)) and 300 ppb NO₂, 0.5 ppb NO, 0.5 ppb O₃ (3(d)).

Figures 4(a) and 4(b) shows the ozone, nitrogen monoxide and nitrogen dioxide traces with time in response to repeating patterns of 40 seconds in the dark and 40 seconds of photolysis. In the case of Figure 4(a), the starting concentrations are 90 ppb NO₂, 30 ppb NO and 50 ppb O₃. In the case of Figure 4(b) the starting concentrations are 10 ppb NO₂, 30 ppb NO and 50 ppb O₃. In Figure 4(c) the starting concentrations are 30 ppb NO₂, 10 ppb NO and 50 ppb O₃. Figure 4(d) shows the corresponding situation for a periodicity of 20 seconds in the dark then 20 seconds photolysis.

Ozone levels can be monitored throughout the reaction to give a time course or, alternatively, the ultraviolet light source can be pulsed for different durations and individual readings taken after each duration pulse then used to form the equivalent time course.

This system can therefore readily establish the concentrations of nitrogen monoxide, nitrogen dioxide and ozone concentrations without needing to pre-treat the sample or wait for a steady state to be reached. (Oxygen is essentially constant and in excess). Prior art methodology measures only a steady state ozone concentration after prolonged irradiation and requires two gases to be scrubbed to make the calculation possible. However, by making three or more independent measurements in different conditions, all three gases can be established without having to scrub the input gas sample.

Examples of suitable ultraviolet sources 4 would be a fluorescent xenon tube, mercury lamp, deuterium lamp, sunlight (perhaps focused through a lens into a reflective cavity), frequency doubled laser or future
5 ultraviolet light source. Indeed, a violet / ultraviolet light emitting diode / diode laser would be ideal if practical devices of this type become available. An ultraviolet light photosensor may be provided to quantify ultraviolet light produced.

10 Several different types of ozone sensor would be suitable. For example, the amperometric type using an aqueous electrolyte and operating at room temperature. Such sensors can be obtained from EN-SCI Inc of Boulder, Colorado, USA and City Technology Ltd of Portsmouth, UK.
15 Solid state semiconductor sensors with a resistance which changes when exposed to ozone could be used. These operate around 500°C and examples include the LGL52 Ozone sensor from Capteur Ltd of Didcot, UK. Stain tubes which change colour when exposed to ozone may be used. These
20 indicate ozone concentration through the depth to which a colour change occurs but are not particularly accurate. Such devices can be obtained from Drägerwerk GmbH in Lubeck, Germany. Other possible ozone sensors include In_2O_3 coated surface acoustic wave devices and
25 phthalocyanines. Non-aqueous electrolyte amperometric ozone sensors are available from Sensoric GmbH in Bonn, Germany.

In an alternative embodiment, nitrogen dioxide or monoxide might be measured instead by means of a suitable
30 sensor. For example, amperometric nitrogen monoxide and nitrogen dioxide sensors which operate at room temperature are sold by City Technology of Portsmouth, UK.

It will be clear to one skilled in the art that an
35 air sample could be trapped in a volume, irradiated and then monitored in situ; however, it is preferred to maintain a flow of air.

In an alternative embodiment, instead of altering the length of time for which a gas sample is irradiated, the equilibrium between nitrogen monoxide and nitrogen dioxide may be altered by other equilibrium altering means. Therefore, instead of or combined with an ultraviolet light source, there may be provided any other means for affecting the equilibrium between nitrogen dioxide and nitrogen monoxide. For example, nitrogen dioxide, nitrogen monoxide or ozone could be added by a gas source or removed by a scrubber. Nitrogen dioxide, nitrogen monoxide or ozone could undergo a chemical reaction, including for example conversion of nitrogen dioxide to nitrogen monoxide using a heated coil, e.g. of platinum/rhodium. Temperature and pressure, can also affect the equilibrium and these can be varied to give different treatments of the gas sample and therefore measurements of equilibrium with different values of J and k_1 . The different position of the equilibrium and/or different characteristic relaxation time under different conditions provides further independent measurements which can be used to calculate all three gas concentrations.

Although calculations are shown which involve the intermediate step of calculating equilibrium steady state concentration of ozone and characteristic time to equilibrium, it will be immediately clear to one skilled in the art that equivalent mathematical calculations may be used to give the required sample gas concentrations and a particular method of calculation can be selected by one skilled in the art.

It may further be taken into account in the calculations that incoming nitrogen monoxide and nitrogen dioxide will be in equilibrium already, although this depends on the ambient ultraviolet level. Given that air oxygen is present in a constant excess (albeit one which varies with altitude) this further constraint could improve the accuracy of the calculations. In this case an external ultraviolet light photosensor might be used

to quantify the level of ultraviolet light experienced externally by the gas sample.

Further sensors, such as an ozone sensor (not shown) besides the inlet **2** may allow further accuracy, although
5 this is not required in the present invention.

It will be clear that a controlled rate of gas flow through the sensor is important. In weather balloons, the weight of a conventional pump is prohibitive.

Referring to figure 5, a sensing apparatus **101**
10 according to the invention is configured to be attached to a weather balloon (not shown) so that, in use, it can be drawn up through the atmosphere by the weather balloon. The arrow in the diagram indicates the direction of air flow through the sensing apparatus **101**
15 when in use. The sensing apparatus **101** has a gas conducting member **102** which has a shape such that its diameter in its central portion is less than that at either of its ends. Such a configuration generates, in use, a region of low pressure in the central narrow
20 region of the gas conducting member **102** by the well-known Venturi effect. It will be recognised by one skilled in the art that many configurations of gas conducting member **102** would provide said region of low pressure, although an elongate pipe is preferred, particularly broadly
25 cylindrical hourglass- shaped pipe.

In the central region there is positioned a sensor element **103** and a shield member **104** which protects the sensor element **103** from damage due to hailstones, heavy rain, etc during use. The shield **104** is arranged such
30 that it connects to the central region of the gas conducting member **102**. In use, the low pressure region generated in the gas conducting member **102** draws air into the shield **104** and over the sensor element **103** using, for example, King's Law. In this example the sensor element
35 **103** is an ozone detector but it is also possible to detect other atmospheric matter.

The shield member **104** maybe connected directly to the external outlet **7** of the sensor shown in Figure 1 but

this sensing apparatus 100 may be used with any type of sensor element 103 for detection of different gases.

Instead of using a low pressure region to draw air through the shield 104, the invention also encompasses
5 the use of a high pressure region to drive air through the shield 104 and past the sensor element 103. Figure 7 shows an example of a gas conducting member which provides such a high pressure region. Components corresponding to those in figure 5 are numbered
10 identically. In this example a constricting member is provided at what is, in use, the lower end of gas conducting member 102. The constriction has a narrow opening 108 and tapered base to allow particles such as rain and ice to fall out of the cylindrical member 102,
15 but is narrow enough to direct air through the shield 104 and over sensor 103. Other configurations of gas conducting member to provide low or high pressure regions will now be apparent to one skilled in the art.

Figure 8 shows a detail of a sensor element 103 in a shield 104. In this example the air flow over the sensor
20 element 103 may be generated by a device shown in figures 5 to 7 or by more conventional positioning of the sensor element within a known sensor manifold. It does, however, have particular benefits in the configuration
25 shown in figures 5 to 7.

Many sensors elements are sensitive to air flow and it is important to know to be able to either fix or measure the air flow past such sensors. It is desirable to do this in such a fashion as to minimise the number,
30 cost and weight of instruments and apparatus.

Some sensor elements, particularly tungsten oxide detectors for ozone have to be maintained at a high temperature relative to the surrounding air. For example, a tungsten oxide sensor will typically be
35 maintained between 500 - 600 °C in air which is between 200 and 300 °K. These sensors are mounted on hot wires and the power supplied to the sensors is altered using

standard feedback techniques to maintain sensor element temperature.

In this example, the sensor element **103** is supported by electrical connecting wire **106** which connects to a sensor driving and monitoring device **107**. The wires provide electrical energy to a heating element **108** on the sensor **103** or adjacent to the sensor element **103** itself, causing the sensor element **103** to be heated as is standard. Airflow over the sensor element **103** when the sensor **101** is in use cools the sensor element **103** and the actual temperature of the sensor element **103** can be determined by a temperature sensor **109**.

However, as the primary source of cooling of the sensor element **103** is the passing air and as this depends in a calculable relationship on the speed of the passing air, this invention recognises that the amount of power required to maintain the temperature of the sensor can be used to calculate the rate of cooling of the sensor due to passing air and therefore the speed of said passing air.

This air flow data is useful not just to improve the accuracy of readings from the sensor element **103** but also for determining other operating parameters.

Further alterations and modifications may be made within the scope of the invention herein disclosed. Accordingly, the scope of the present invention should be construed solely by reference to the appended claims.

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